Probing plasmon resonances and local optical fields of SERS-active metal nanostructures

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Probing plasmon resonances and local optical fields of SERS-active metal nanostructures

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Collective oscillations of the free electrons in metal nanostructures, called surface plasmons can strongly couple to light. This coupling gives rise to high local fields in the vicinity of such structures Surface enhanced Raman scattering (SERS) is probably one of the most exciting examples to demonstrate the capabilities and the potential of spectroscopy performed in enhanced local fields. By exploiting so-called “hot spots”, i.e. areas in nm dimension showing extremely high local fields, SERS enables molecular structural characterizations of molecules at single molecule level [1]. Vice versa, spectroscopy suggests sensitive probing of local fields where a single molecule can act as a tiny (sub)nano-sensor.

Here we investigate various plasmonic nanostructures by 1- and 2-photon excited SERS [2] and by electron energy loss spectroscopy (EELS) [3]. Compared to optical methods, EELS can provide up to three orders of magnitude better spatial resolution. EELS spectra also allow us to monitor the transition of plasmonic dimers from a classical to a quantum system by decreasing gap widths to dimensions when tunneling between the silver spheres occurs and a conductive nanobridge evolves [4]. In particular, EELS can probe bright and also dark plasmon modes. Figure 1 demonstrates this by displaying the surface plasmon resonances for an isolated silver sphere and a silver dimer.

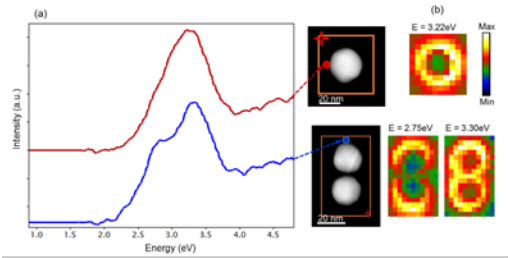

Figure 1 EEL spectra and images of EELS signal intensities in a specific energy window [5].

EELS signals measured at different locations in the vicinity of the dimer appear at very different intensities. Our studies reveal the relation between local fields employed in optical spectroscopy and electron energy-loss. and verify experimentally the predicted increase of local optical fields in the hot spots with decreasing photon energy [2].

We have also observed strong surface enhanced Raman scattering signals for molecules on discontinuous aluminum films using near-infrared (NIR) excitation even though this metal suggests plasmon supported spectroscopy in the ultraviolet range [5].

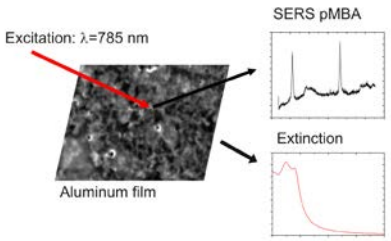

Figure 2 NIR- excited SERS from pMBA on aluminum films [5].

This observation correlates with plasmon resonances in the NIR- range identified in electron energy loss spectra collected from these Al-films.

Out studies show that EEL spectra measured from plasmonic nanostrcutures give a rationale for high SERS enhancement level obtained for excitation in the NIR by identifying plasmon resonances at energies in agreement with NIR wavelengths employed in 1- and 2-photon excited SERS experiments.

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